



# Selective catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub> over CeO<sub>2</sub> supported on TiO<sub>2</sub>: Comparison of anatase, brookite, and rutile

Xiaojiang Yao<sup>a,b,\*</sup>, Ruidun Zhao<sup>c</sup>, Li Chen<sup>a</sup>, Jun Du<sup>c</sup>, Changyuan Tao<sup>c</sup>, Fumo Yang<sup>a,b,\*</sup>, Lin Dong<sup>d</sup>

<sup>a</sup> Research Center for Atmospheric Environment, Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing 400714, PR China

<sup>b</sup> Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, PR China

<sup>c</sup> School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, PR China

<sup>d</sup> Jiangsu Key Laboratory of Vehicle Emissions Control, Center of Modern Analysis, Nanjing University, Nanjing 210093, PR China

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## ABSTRACT

Anatase (A) TiO<sub>2</sub> is widely used as a support of the supported vanadium-based and non-vanadium-based catalysts for NH<sub>3</sub>-SCR reaction. However, there is lack of enough attention for brookite (B) and rutile (R) TiO<sub>2</sub>. Therefore, in the present work, we synthesize a series of TiO<sub>2</sub>-A, TiO<sub>2</sub>-B, and TiO<sub>2</sub>-R, and then used as supports to prepare CeO<sub>2</sub>/TiO<sub>2</sub>-A, CeO<sub>2</sub>/TiO<sub>2</sub>-B, and CeO<sub>2</sub>/TiO<sub>2</sub>-R catalysts with the purpose of clarifying the crystal form effect of TiO<sub>2</sub> supports on the physicochemical properties and catalytic performance of these supported ceria-based catalysts for NH<sub>3</sub>-SCR reaction. Characterization results exhibit that H<sub>2</sub> consumption (responding to reduction property), acid amounts, surface Ce<sup>3+</sup> content, surface adsorbed oxygen species, and catalytic performance of these supported ceria-based catalysts give the order of CeO<sub>2</sub>/TiO<sub>2</sub>-R > CeO<sub>2</sub>/TiO<sub>2</sub>-B > CeO<sub>2</sub>/TiO<sub>2</sub>-A, which is related to the interaction (i.e., Ce<sup>3+</sup> + Ti<sup>4+</sup> ↔ Ce<sup>4+</sup> + Ti<sup>3+</sup>) between CeO<sub>2</sub> and TiO<sub>2</sub> (anatase, brookite, and rutile). Especially, CeO<sub>2</sub>/TiO<sub>2</sub>-R catalyst exhibits the optimal catalytic performance for NH<sub>3</sub>-SCR reaction among these supported ceria-based catalysts owing to the most excellent reduction property as well as the largest amounts of acid sites, surface Ce<sup>3+</sup> content, and surface adsorbed oxygen species.

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## 1. Introduction

V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub>/TiO<sub>2</sub> catalysts are practically applied for the selective catalytic reduction of nitrogen oxides (NO<sub>x</sub>) by NH<sub>3</sub> (NH<sub>3</sub>-SCR) to control the emission of NO<sub>x</sub> from stationary sources (such as coal-fired power plants), which is because of their good catalytic performance and excellent resistance to SO<sub>2</sub> [1–5]. As early as 1994, Topsøe et al. [6] pointed out that the catalytic cycle of NH<sub>3</sub>-SCR consists redox and acid cycles over vanadium-based catalysts based on transient or steady-state *in situ* Fourier transform infrared spectroscopy (FTIR) experiments. In addition, it is well known that with regard to V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub>/TiO<sub>2</sub> catalysts, V<sub>2</sub>O<sub>5</sub> is the main redox active site, WO<sub>3</sub> (or MoO<sub>3</sub>) provides surface acidity, and TiO<sub>2</sub> is used as a support

with superior resistance to SO<sub>2</sub> [1,7]. However, there are some disadvantages in this kind of catalysts, such as the biological toxicity of V<sub>2</sub>O<sub>5</sub>, narrow operating temperature window, generation of large amount of N<sub>2</sub>O at high temperature, and high activity for the oxidation of SO<sub>2</sub> to SO<sub>3</sub>, etc. [8–10]. Therefore, it is very significant to develop a novel environment-friendly non-vanadium-based catalyst with excellent catalytic performance and high resistance to SO<sub>2</sub> for NH<sub>3</sub>-SCR.

In recent years, ceria (CeO<sub>2</sub>) has been widely investigated in NH<sub>3</sub>-SCR reaction due to its good redox property and high storage/release oxygen capacity, associated with the abundant oxygen vacancy and facile shift of Ce<sup>3+</sup>/Ce<sup>4+</sup> [11–13]. Pure CeO<sub>2</sub> exhibits poor NH<sub>3</sub>-SCR reactivity, but its catalytic performance can be remarkably enhanced by the following two approaches [14–17]: (1) combining with other metal-oxides to synthesize ceria-based mixed-oxide catalysts; and (2) highly dispersed on the surface of supports to prepare supported ceria-based catalysts. For example, He et al. [15] synthesized a CeO<sub>2</sub>-TiO<sub>2</sub> mixed-oxide catalyst through an optimized homogeneous precipitation method, and found that its catalytic performance is better than that of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>

\* Corresponding authors at: Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Fangzheng Avenue 266#, Chongqing 400714, PR China. Tel.: +86 23 65935909; fax: +86 23 65935924.

E-mail addresses: [yaouxj@cigit.ac.cn](mailto:yaouxj@cigit.ac.cn) (X. Yao), [fmyang@cigit.ac.cn](mailto:fmyang@cigit.ac.cn) (F. Yang).

catalyst for  $\text{NH}_3$ -SCR due to the synergistic effect between  $\text{CeO}_2$  and  $\text{TiO}_2$ . Li et al. [10] reported that  $\text{CeO}_2/\text{TiO}_2\text{-SiO}_2$  catalysts prepared by a wet impregnation method exhibited excellent  $\text{NH}_3$ -SCR reactivity, high  $\text{N}_2$  selectivity, and good resistance to  $\text{SO}_2$  and  $\text{H}_2\text{O}$ , which is attributed to the highly dispersion of  $\text{CeO}_2$  on the surface of  $\text{TiO}_2\text{-SiO}_2$  support, the conversion of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$ , and the increase of Brønsted (B) acid sites.

As mentioned above,  $\text{TiO}_2$  has superior resistance to  $\text{SO}_2$ , so it is widely used as a support of non-vanadium-based catalysts for  $\text{NH}_3$ -SCR [18–20]. It is well known that  $\text{TiO}_2$  consists three crystal forms of anatase, brookite, and rutile. In the past years, the crystal form effect of  $\text{TiO}_2$  on the catalytic performance of titanium-based catalysts has been deeply discussed for some photocatalytic reactions, such as photocatalytic reduction of  $\text{CO}_2$ , photocatalytic oxygen evolution, photocatalytic hydrogen production, and photocatalytic degradation of water pollutants, etc. [21–27]. As we all know that anatase usually exhibits better photocatalytic activity than that of brookite and rutile. Nevertheless, there are numerous examples for the unexpectedly high activity of brookite and rutile. For example, Li et al. [28] prepared a series of anatase, brookite, and rutile  $\text{TiO}_2$  catalysts for photocatalytic reduction of  $\text{CO}_2$ , and found that helium (He) pretreatment of these catalysts at a moderate temperature led to the generation of oxygen vacancy and  $\text{Ti}^{3+}$  on the surface of anatase and brookite except rutile. Furthermore, they pointed out that the photocatalytic performance of defective brookite is better than that of anatase and rutile due to the lowest formation energy of oxygen vacancy on the surface of brookite. Macyk et al. [29] compared the photocatalytic performance of anatase and rutile  $\text{TiO}_2$  for oxygen activation, and reported that rutile is a good photocatalyst for the activation of molecular oxygen because that more efficient  $\text{O}_2^{\bullet-}$  production happens on the surface of rutile, which is related to the good adsorption of oxygen and the low redox potential of the excited electron. However, the crystal form effect of  $\text{TiO}_2$  on the catalytic performance of the supported non-vanadium-based catalysts for  $\text{NH}_3$ -SCR has not yet been reported. In view of the successful application of anatase  $\text{TiO}_2$  in  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  and  $\text{V}_2\text{O}_5\text{-MoO}_3/\text{TiO}_2$  catalysts for  $\text{NH}_3$ -SCR, the current investigation of  $\text{TiO}_2$  supports for the supported non-vanadium-based denitration catalysts is mainly focused on anatase. Therefore, it is necessary to carry out a comparative research about anatase, brookite, and rutile supporting non-vanadium-based denitration catalysts.

In the present work, we synthesized a series of anatase, brookite, and rutile  $\text{TiO}_2$ , and then used as supports to prepare the supported ceria-based catalysts for  $\text{NH}_3$ -SCR. The obtained samples were characterized by means of XRD, Raman,  $\text{N}_2$ -physisorption,  $\text{H}_2$ -TPR,  $\text{NH}_3$ -TPD, *in situ* DRIFTS, XPS, and  $\text{NH}_3$ -SCR model reaction with the purpose of exploring the crystal form effect of  $\text{TiO}_2$  on the physicochemical properties and catalytic performance of  $\text{CeO}_2/\text{TiO}_2$  catalysts for  $\text{NH}_3$ -SCR.

## 2. Experimental section

### 2.1. Catalysts preparation

Three crystal forms of  $\text{TiO}_2$  were respectively prepared by precipitation, hydrothermal treatment, and sol-gel methods according to the literatures [13,28]. To prepare anatase  $\text{TiO}_2$ , the required amount of  $\text{TiCl}_4$  was dissolved in distilled water (containing 1% v/v concentrated HCl) with magnetic stirring during an ice-water bath. And then, ammonia (25%) was dropwisely added into the above  $\text{TiCl}_4$  solution with magnetic stirring until pH = 10. The resulting suspension was kept in stirring for another 3 h, aged 24 h, and subsequently filtered, washed several times with distilled water until pH = 7 and no  $\text{Cl}^-$  detected by  $\text{AgNO}_3$ . For brookite  $\text{TiO}_2$ , the desired amount of titanium(IV) bis(ammonium lactato) dihydroxide (TALH,

$\text{C}_6\text{H}_{18}\text{N}_2\text{O}_8\text{Ti}$ ) aqueous solution (50%) and a quantitative amount of 7 M urea were dissolved in distilled water and mixed together with magnetic stirring for 1 h. The resulting solution was transferred into a Teflon-lined autoclave, and then heated from room temperature to 160 °C and held for 24 h in an oven. After that, the autoclave was naturally cooled to room temperature in static air. The precipitate was filtered and washed several times with distilled water until pH = 7. With regard to rutile  $\text{TiO}_2$ , the desired amount of  $\text{TiCl}_4$  was dropwisely added into the absolute ethanol with magnetic stirring for 1 h to form a transparent yellowish sol. And then, the obtained sol was slowly added into distilled water with magnetic stirring for another 1 h. In which, the molar ratio of  $\text{TiCl}_4$ , absolute ethanol, and distilled water was fixed at 1:10:140. After that, the solution was kept in a closed system at 50 °C for 24 h in an oven to obtain a yellowish gel. The resulting gel was naturally cooled to room temperature in static air, and then filtered, washed several times with distilled water until pH = 7 and no  $\text{Cl}^-$  detected by  $\text{AgNO}_3$ . Finally, all of these obtained cakes were oven dried at 110 °C overnight and subsequently calcined at 400 °C in the flowing air for 5 h. The prepared anatase, brookite, and rutile  $\text{TiO}_2$  samples were denoted as  $\text{TiO}_2\text{-A}$ ,  $\text{TiO}_2\text{-B}$ , and  $\text{TiO}_2\text{-R}$ , respectively.

The supported ceria-based catalysts were prepared by incipient-wetness impregnating the  $\text{TiO}_2\text{-A}$ ,  $\text{TiO}_2\text{-B}$ , and  $\text{TiO}_2\text{-R}$  supports with  $\text{Ce}(\text{NO}_3)_3$  solution. The mixture was kept in magnetic stirring for 1 h and evaporated to remove water at 110 °C during an oil bath. The obtained samples were oven dried at 110 °C overnight, and finally calcined at 400 °C for 5 h in the flowing air. Furthermore, the loading amount of  $\text{CeO}_2$  was fixed at 0.4 mmol  $\text{CeO}_2/\text{g}$ -support. The prepared catalysts were denoted as  $\text{CeO}_2/\text{TiO}_2\text{-A}$ ,  $\text{CeO}_2/\text{TiO}_2\text{-B}$ , and  $\text{CeO}_2/\text{TiO}_2\text{-R}$ , respectively.

### 2.2. Catalysts characterization

X-ray diffraction (XRD) patterns of these samples were recorded on a Philips X'Pert3 Powder diffractometer using Ni-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15418$  nm). The operating voltage and current of X-ray tube were fixed at 40 kV and 40 mA. The scan speed was set at  $10^\circ \text{min}^{-1}$  with a step size of  $0.02^\circ$ . The intensity data were collected from  $2\theta = 10$  to  $80^\circ$ .

Raman spectra of these samples were collected on a Renishaw inVia Reflex Laser Raman spectrometer using  $\text{Ar}^+$  laser beam. The excitation wavelength was 532 nm and the laser power was 5 mW. The intensity data were collected from 100 to  $1000 \text{ cm}^{-1}$ .

Textural characteristics of these samples were obtained by  $\text{N}_2$ -physisorption at  $-196^\circ\text{C}$  on a Belsorp-max analyzer, choosing Brunauer-Emmet-Teller (BET) method for calculating the specific surface area in the relative pressure range of  $P/P_0 = 0\text{--}0.3$ , and using Barrett-Joyner-Halenda (BJH) method for obtaining the pore distribution. Prior to each analysis, the sample was degassed under vacuum at 300 °C for 4 h.

$\text{H}_2$ -temperature programmed reduction ( $\text{H}_2$ -TPR) experiments were performed in a quartz reactor connected to a thermal conductivity detector (TCD) with  $\text{H}_2\text{-Ar}$  mixture (7.0%  $\text{H}_2$  by volume,  $30 \text{ ml min}^{-1}$ ) as a reductant. Prior to the reduction, the catalyst (50 mg) was pretreated in high purified  $\text{N}_2$  at 300 °C for 1 h, and then cooled to ambient temperature. After that, the  $\text{H}_2$ -TPR started from 100 to 900 °C at a rate of  $10^\circ\text{C min}^{-1}$ . The curve fitting was performed by using Origin 8.0 with a plugin of Peak Fitting Module (PFM). Furthermore,  $\text{H}_2$  consumption of these samples was calibrated by  $\text{CuO}$  standard sample according to the calculation of peak area.

$\text{NH}_3$ -temperature programmed desorption ( $\text{NH}_3$ -TPD) experiments were carried out on a dynamic chemisorption analyzer with a quartz reactor, detected by a thermal conductivity detector (TCD). About 200 mg catalyst was pretreated by high purified  $\text{N}_2$  ( $30 \text{ ml min}^{-1}$ ) at 300 °C for 1 h. After pretreatment, the catalyst was

saturated with  $\text{NH}_3\text{-N}_2$  mixture (1.0%  $\text{NH}_3$  by volume,  $30\text{ ml min}^{-1}$ ) at  $100^\circ\text{C}$  for 1 h and subsequently flushed with high purified  $\text{N}_2$  ( $30\text{ ml min}^{-1}$ ) at the same temperature for 1 h to remove the gaseous  $\text{NH}_3$ , and then cooled to ambient temperature. After that, the catalyst was heated from ambient temperature to  $800^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$  in high purified  $\text{N}_2$  ( $30\text{ ml min}^{-1}$ ). The curve fitting was performed by using Origin 8.0 with a plugin of Peak Fitting Module (PFM).

*In situ* diffuse reflectance infrared Fourier transform spectra of  $\text{NH}_3$ -adsorption ( $\text{NH}_3$ -adsorption *in situ* DRIFTS) over these catalysts were collected on a Nicolet 5700 FT-IR spectrometer equipped with a high-sensitive MCT detector cooled by liquid  $\text{N}_2$ . The catalyst was placed in an *in situ* DRIFTS cell (Harrick) and pretreated by high purified  $\text{N}_2$  at  $450^\circ\text{C}$  for 1 h to remove the physisorbed water. The sample background of each target temperature was collected during the cooling process. At room temperature, the sample was exposed to  $\text{NH}_3\text{-N}_2$  mixture (1.0%  $\text{NH}_3$  by volume) at a rate of  $50\text{ ml min}^{-1}$  for 1 h to be saturated. And then, the gaseous  $\text{NH}_3$  was purged by high purified  $\text{N}_2$  ( $50\text{ ml min}^{-1}$ ) for 1 h at the same temperature. *In situ* DRIFTS were recorded at various target temperatures from room temperature to  $450^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$  in high purified  $\text{N}_2$  by subtraction of the corresponding sample background.

X-ray photoelectron spectra (XPS) of these catalysts were performed on a PHI 5000 VersaProbe system, using monochromatic Al  $\text{K}\alpha$  radiation (1486.6 eV) operating at an accelerating power of 15 kW. Before the measurement, the catalyst was outgassed at room temperature in a UHV chamber ( $<5 \times 10^{-7}\text{ Pa}$ ). The sample charging effects were compensated by calibrating all binding energies (BE) with the adventitious C 1s peak at 284.6 eV. The curve fitting was performed by using XPSPEAK 4.1 with a Shirley-type background.

### 2.3. Catalytic performance measurement

The catalytic performance of these  $\text{TiO}_2$  supports and supported ceria-based catalysts for  $\text{NH}_3\text{-SCR}$  model reaction was determined under steady state, involving a feed stream with a fixed composition of 500 ppm NO, 500 ppm  $\text{NH}_3$ , 5%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$  (when used), 100 ppm  $\text{SO}_2$  (when used), and  $\text{N}_2$  in balance. The catalyst (400 mg) was fitted in a quartz tube and pretreated with high purified  $\text{N}_2$  at  $300^\circ\text{C}$  for 1 h and then cooled to room temperature, after that, the mixed reaction gases were switched on. The reactions were carried out at different temperatures with a space velocity of  $60000\text{ ml g}^{-1}\text{ h}^{-1}$ . NO and  $\text{NO}_2$  concentrations of inlet and outlet were detected by a flue gas analyzer.  $\text{N}_2\text{O}$  concentration was measured by a  $\text{N}_2\text{O}$  analyzer. And  $\text{NO}_x$  conversion was calculated from the following equation:

$$\text{NO}_x \text{ conversion}(\%) = \frac{[\text{NO}]_{\text{in}} + [\text{NO}_2]_{\text{in}} - [\text{NO}]_{\text{out}} - [\text{NO}_2]_{\text{out}}}{[\text{NO}]_{\text{in}} + [\text{NO}_2]_{\text{in}}} \times 100\%$$

## 3. Results and discussion

### 3.1. Structural and textural characteristics (XRD, Raman, and $\text{N}_2$ -physisorption)

The crystal form of  $\text{TiO}_2$  and the dispersion state of  $\text{CeO}_2$  are determined by XRD, and the corresponding results are displayed in Fig. 1.  $\text{TiO}_2\text{-A}$  exhibits a series diffraction peaks at  $25.28^\circ$ ,  $36.95^\circ$ ,  $37.81^\circ$ ,  $38.58^\circ$ ,  $48.05^\circ$ ,  $54.04^\circ$ ,  $55.10^\circ$ ,  $62.69^\circ$ ,  $68.76^\circ$ ,  $70.31^\circ$ , and  $75.13^\circ$ , which are attributed to anatase [PDF-ICDD 21-1272].  $\text{TiO}_2\text{-B}$  presents the characteristic peaks at  $25.63^\circ$ ,  $30.87^\circ$ ,  $32.80^\circ$ ,  $36.33^\circ$ ,  $37.38^\circ$ ,  $40.20^\circ$ ,  $42.45^\circ$ ,  $46.16^\circ$ ,  $48.09^\circ$ ,  $49.25^\circ$ ,  $52.17^\circ$ ,  $54.32^\circ$ ,  $55.32^\circ$ ,  $57.25^\circ$ , and so on, which are ascribed to brookite [PDF-ICDD 29-1360].

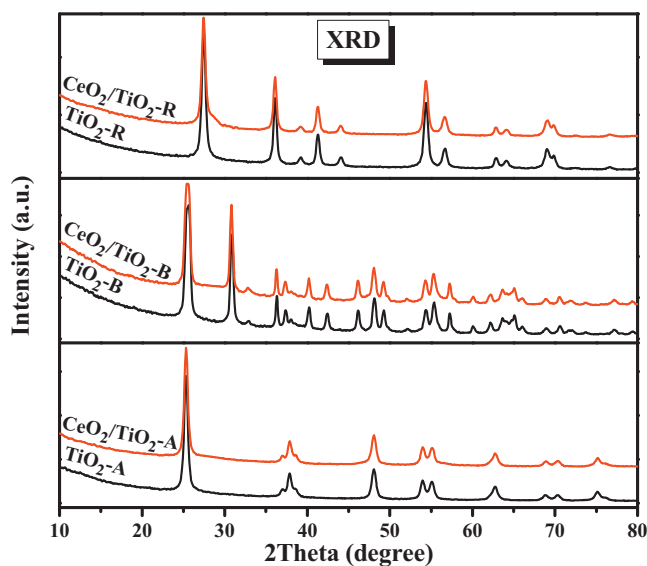


Fig. 1. XRD patterns of these supports and the corresponding supported ceria-based catalysts.

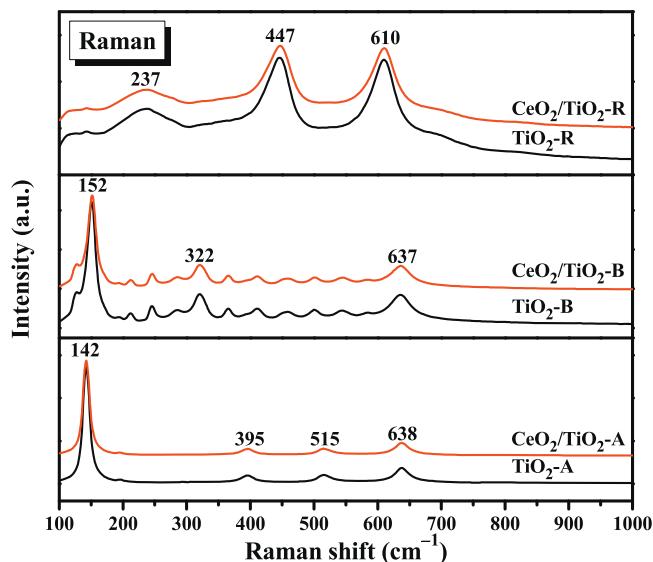
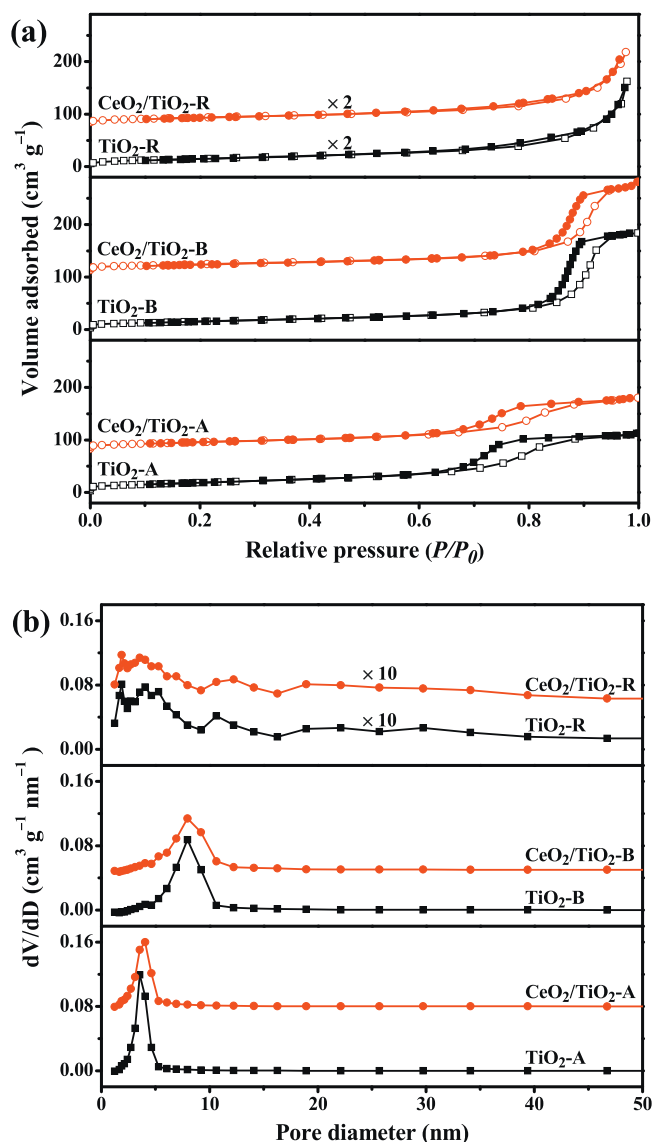


Fig. 2. Raman spectra of these supports and the corresponding supported ceria-based catalysts.

$\text{TiO}_2\text{-R}$  displays its diffraction peaks at  $27.45^\circ$ ,  $36.11^\circ$ ,  $39.20^\circ$ ,  $41.24^\circ$ ,  $44.06^\circ$ ,  $54.38^\circ$ ,  $56.64^\circ$ ,  $62.82^\circ$ ,  $64.04^\circ$ ,  $69.00^\circ$ , and  $69.83^\circ$ , which are assigned to rutile [PDF-ICDD 21-1276]. The obtained results indicate that three crystal forms of  $\text{TiO}_2$  (i.e., anatase, brookite, and rutile) have been successfully synthesized in the present work. It can be seen from Fig. 1 that the XRD patterns of these supported ceria-based catalysts are very similar with the corresponding  $\text{TiO}_2$  supports, and no diffraction peaks of  $\text{CeO}_2$  [PDF-ICDD 34-0394] can be detected. Furthermore, we can find that the peak intensity of  $\text{CeO}_2/\text{TiO}_2\text{-A}$ ,  $\text{CeO}_2/\text{TiO}_2\text{-B}$ , and  $\text{CeO}_2/\text{TiO}_2\text{-R}$  catalysts is weaker than that of the corresponding  $\text{TiO}_2$  supports. These observations suggest that  $\text{CeO}_2$  species is highly dispersed on the surface of  $\text{TiO}_2\text{-A}$ ,  $\text{TiO}_2\text{-B}$ , and  $\text{TiO}_2\text{-R}$  supports [21,30].

Raman spectrum is chosen to further confirm the structure of these  $\text{TiO}_2$  supports and supported ceria-based catalysts, as shown in Fig. 2.  $\text{TiO}_2\text{-A}$  gives four Raman bands at 142, 395, 515, and  $638\text{ cm}^{-1}$ , which is consistent with the Raman spectrum of anatase [13,28].  $\text{TiO}_2\text{-B}$  exhibits a series of complex Raman bands, which are



**Fig. 3.** (a) N<sub>2</sub> adsorption-desorption isotherms and (b) BJH pore distribution curves of these supports and the corresponding supported ceria-based catalysts.

related to brookite, and the strongest three Raman bands appear at 152, 322, and 637 cm<sup>-1</sup> [27,28]. TiO<sub>2</sub>-R presents three Raman bands at 237, 447, and 610 cm<sup>-1</sup>, which indicates a rutile structure [21,27]. These experimental results are in well agreement with XRD, and further confirm that we have successfully synthesized anatase, brookite, and rutile TiO<sub>2</sub> supports. Simultaneously, Raman spectra of these supported ceria-based catalysts are very similar with those of the corresponding TiO<sub>2</sub> supports, and F<sub>2g</sub> Raman vibration mode of CeO<sub>2</sub> is absent. Moreover, the Raman band intensity of the catalysts is obviously weaker than that of supports, which suggests that the high dispersion of CeO<sub>2</sub> species on the surface of TiO<sub>2</sub>-A, TiO<sub>2</sub>-B, and TiO<sub>2</sub>-R covers these supports and weakens the signals.

Fig. 3 displays N<sub>2</sub> adsorption-desorption isotherms and BJH pore distribution curves of these TiO<sub>2</sub> supports and the corresponding supported ceria-based catalysts. It can be seen from Fig. 3(a) that all of these samples exhibit the classical IV-type isotherm with an obvious type H1 (for TiO<sub>2</sub>-A, TiO<sub>2</sub>-B, CeO<sub>2</sub>/TiO<sub>2</sub>-A, and CeO<sub>2</sub>/TiO<sub>2</sub>-B) or H3 (for TiO<sub>2</sub>-R and CeO<sub>2</sub>/TiO<sub>2</sub>-R) hysteresis loop as defined by IUPAC, which indicates that mesopore (2–50 nm) structure exists in these samples [19,21,31]. The mesopore structure of these

**Table 1**

BET specific surface area, total pore volume, and mean pore diameter of these supports and the corresponding supported ceria-based catalysts.

Samples	BET specific surface area (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Mean pore diameter (nm)
TiO <sub>2</sub> -A	70.8	0.1871	10.6
TiO <sub>2</sub> -B	57.6	0.2981	20.7
TiO <sub>2</sub> -R	28.9	0.1257	17.4
CeO <sub>2</sub> /TiO <sub>2</sub> -A	59.6	0.1711	11.5
CeO <sub>2</sub> /TiO <sub>2</sub> -B	53.0	0.2623	19.8
CeO <sub>2</sub> /TiO <sub>2</sub> -R	25.7	0.1223	19.1

samples is formed by the agglomeration or compaction of particles [31]. Type H1 hysteresis loop of TiO<sub>2</sub>-A, TiO<sub>2</sub>-B, CeO<sub>2</sub>/TiO<sub>2</sub>-A, and CeO<sub>2</sub>/TiO<sub>2</sub>-B suggests their uniform and narrow distributions of pore size, while Type H3 hysteresis loop of TiO<sub>2</sub>-R and CeO<sub>2</sub>/TiO<sub>2</sub>-R indicates their slit-shaped pores formed by the agglomeration of plate-like particles [31]. Indeed, Fig. 3(b) exhibits that the pore size distributions of TiO<sub>2</sub>-A, TiO<sub>2</sub>-B, CeO<sub>2</sub>/TiO<sub>2</sub>-A, and CeO<sub>2</sub>/TiO<sub>2</sub>-B are obviously better and narrower than those of TiO<sub>2</sub>-R and CeO<sub>2</sub>/TiO<sub>2</sub>-R, while all of them are located in mesopore range. The textural data of these samples are listed in Table 1. We can find that the BET specific surface area of TiO<sub>2</sub>-A, TiO<sub>2</sub>-B, and TiO<sub>2</sub>-R is 70.8, 57.6, and 28.9 m<sup>2</sup> g<sup>-1</sup>, respectively. With the loading of CeO<sub>2</sub> on the surface of these TiO<sub>2</sub> supports, the BET specific surface area decreases to 59.6, 53.0, and 25.7 m<sup>2</sup> g<sup>-1</sup>, respectively. Furthermore, the total pore volume of TiO<sub>2</sub>-A and TiO<sub>2</sub>-B decreases obviously after the introduction of CeO<sub>2</sub>, which indicates that CeO<sub>2</sub> is mainly located at the bottom of mesopores. However, the total pore volume of TiO<sub>2</sub>-R has no obvious change before and after the loading of CeO<sub>2</sub>, suggesting that CeO<sub>2</sub> mainly locates on the outer surface of TiO<sub>2</sub>-R.

### 3.2. Reduction behavior (H<sub>2</sub>-TPR)

H<sub>2</sub>-TPR is used to investigate the reduction properties of these supported ceria-based catalysts, as shown in Fig. 4. Moreover, the results of TiO<sub>2</sub>-A, TiO<sub>2</sub>-B, and TiO<sub>2</sub>-R supports, as well as pure CeO<sub>2</sub> are also given in this figure for comparison. It can be seen from Fig. 4(a) that TiO<sub>2</sub>-A, TiO<sub>2</sub>-B, and TiO<sub>2</sub>-R supports exhibit the reduction peak at 571, 677, and 551 °C, respectively. Pure CeO<sub>2</sub> presents two reduction peaks around 507 and 805 °C, which are assigned to the reduction of surface CeO<sub>2</sub> and bulk CeO<sub>2</sub>, respectively [13,14]. In addition, H<sub>2</sub> consumption of TiO<sub>2</sub>-A, TiO<sub>2</sub>-B, TiO<sub>2</sub>-R, and pure CeO<sub>2</sub> is 123, 243, 161, and 1960 μmol g<sup>-1</sup>, which can be used for calculating the theoretical H<sub>2</sub> consumption of CeO<sub>2</sub>/TiO<sub>2</sub>-A, CeO<sub>2</sub>/TiO<sub>2</sub>-B, and CeO<sub>2</sub>/TiO<sub>2</sub>-R catalysts. Interestingly, Fig. 4(b) shows that the H<sub>2</sub>-TPR profiles of CeO<sub>2</sub>/TiO<sub>2</sub>-A, CeO<sub>2</sub>/TiO<sub>2</sub>-B, and CeO<sub>2</sub>/TiO<sub>2</sub>-R catalysts are very similar, all of which exhibit three reduction peaks between 300 and 900 °C, labeled as α, β, and γ, respectively. The low-temperature reduction peak (α) around 500 °C and the high-temperature reduction peak (γ) around 800 °C can be respectively attributed to the reduction of surface dispersed CeO<sub>2</sub> and clustered (bulk-like) CeO<sub>2</sub> [32–34]. And the mid-temperature reduction peak (β) around 650 °C may be ascribed to the reduction of Ce–O–Ti species, which generates from the interaction between CeO<sub>2</sub> and TiO<sub>2</sub>. Furthermore, the reduction peak temperature and H<sub>2</sub> consumption of these supported ceria-based catalysts are summarized in Table 2. Interestingly, the actual H<sub>2</sub> consumption of CeO<sub>2</sub>/TiO<sub>2</sub>-A, CeO<sub>2</sub>/TiO<sub>2</sub>-B, and CeO<sub>2</sub>/TiO<sub>2</sub>-R catalysts is obviously larger than the corresponding theoretical H<sub>2</sub> consumption (shown in the parentheses in Table 2). This phenomenon further confirms that some interaction exists between these TiO<sub>2</sub> supports and the surface dispersed CeO<sub>2</sub>, which can promote the reduction of each other efficiently. Moreover, we can find that the reduction peak temperature of CeO<sub>2</sub>/TiO<sub>2</sub>-R catalyst is obviously lower than that of CeO<sub>2</sub>/TiO<sub>2</sub>-A and CeO<sub>2</sub>/TiO<sub>2</sub>-B catalysts. H<sub>2</sub> consumption of these catalysts



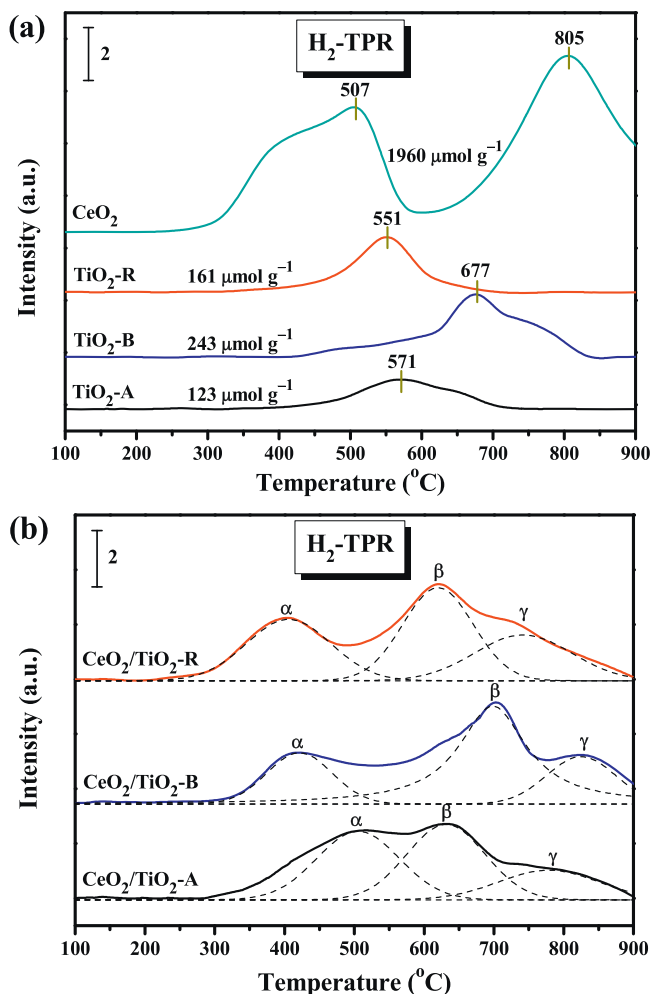


Fig. 4. H<sub>2</sub>-TPR profiles of (a) these TiO<sub>2</sub> supports (and pure CeO<sub>2</sub>), and (b) the corresponding supported ceria-based catalysts.

Table 2

Peak temperature and H<sub>2</sub> consumption of these supported ceria-based catalysts obtained from H<sub>2</sub>-TPR.

Catalysts	Peak temperature (°C)			H <sub>2</sub> consumption (μmol g <sup>-1</sup> )			
	T <sub>α</sub>	T <sub>β</sub>	T <sub>γ</sub>	S <sub>α</sub>	S <sub>β</sub>	S <sub>γ</sub>	S <sub>α</sub> + S <sub>β</sub> + S <sub>γ</sub>
CeO <sub>2</sub> /TiO <sub>2</sub> -A	507	635	792	242	253	92	587 (241)
CeO <sub>2</sub> /TiO <sub>2</sub> -B	421	702	826	143	359	124	626 (354)
CeO <sub>2</sub> /TiO <sub>2</sub> -R	405	620	745	222	281	174	677 (277)

can be ranked by CeO<sub>2</sub>/TiO<sub>2</sub>-R > CeO<sub>2</sub>/TiO<sub>2</sub>-B > CeO<sub>2</sub>/TiO<sub>2</sub>-A. These phenomena indicate that the reduction property of CeO<sub>2</sub>/TiO<sub>2</sub>-R is the best among these catalysts due to the strongest interaction between CeO<sub>2</sub> and TiO<sub>2</sub>-R, which is supported by the theoretical study results of Pan et al. [35]. They reported that the formation energy of Ti<sup>4+</sup> defects is 11.76, 11.19, and 10.86 eV for anatase, brookite, and rutile TiO<sub>2</sub>, respectively, obtained by theoretical calculation. The result suggests that the transfer of Ti<sup>4+</sup> to generate Ti<sup>4+</sup> defects in rutile TiO<sub>2</sub> is the easiest among these crystal forms of TiO<sub>2</sub>. Therefore, it could be deduced that there is the strongest interaction between CeO<sub>2</sub> and TiO<sub>2</sub>-R among these catalysts due to the easiest transfer of Ti<sup>4+</sup> and the subsequent occupation of Ti<sup>4+</sup> defects by Ce<sup>4+</sup> through their interface in the preparation process of CeO<sub>2</sub>/TiO<sub>2</sub>-R catalyst.

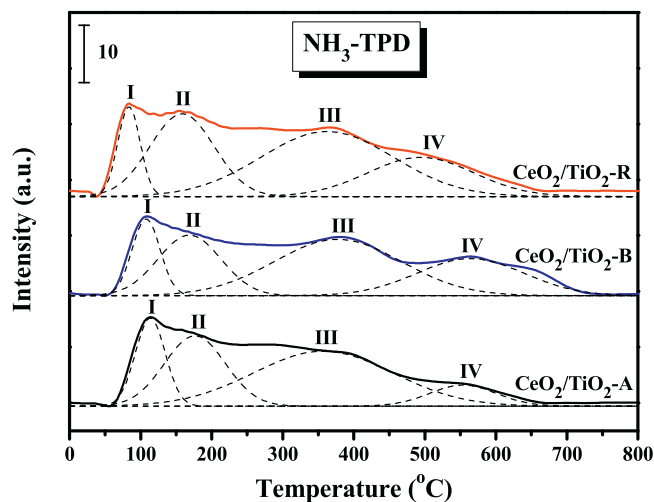


Fig. 5. NH<sub>3</sub>-TPD profiles of these supported ceria-based catalysts.

Table 3

Quantitative analysis of NH<sub>3</sub>-TPD over these supported ceria-based catalysts.

Catalysts	Acid amount (a.u.)				Total acid amount (a.u.)
	S <sub>I</sub>	S <sub>II</sub>	S <sub>III</sub>	S <sub>IV</sub>	S <sub>I</sub> + S <sub>II</sub> + S <sub>III</sub> + S <sub>IV</sub>
CeO <sub>2</sub> /TiO <sub>2</sub> -A	829	1357	2411	446	5043
CeO <sub>2</sub> /TiO <sub>2</sub> -B	676	1200	2253	1239	5368
CeO <sub>2</sub> /TiO <sub>2</sub> -R	634	1669	2715	1306	6324

### 3.3. Surface acid property (NH<sub>3</sub>-TPD and NH<sub>3</sub>-adsorption *in situ* DRIFTS)

Surface acidity of these supported ceria-based catalysts is measured by NH<sub>3</sub>-TPD, and the corresponding results are presented in Fig. 5. It is widely reported that the position and area of the desorption peak are closely related to the strength and amount of surface acid sites over the catalysts, respectively [7,36]. We can see from Fig. 5 that NH<sub>3</sub>-TPD profiles of CeO<sub>2</sub>/TiO<sub>2</sub>-A, CeO<sub>2</sub>/TiO<sub>2</sub>-B, and CeO<sub>2</sub>/TiO<sub>2</sub>-R catalysts are very similar, which exhibit four desorption peaks during the temperature range of measurement, labeled as I, II, III, and IV. These desorption peaks can be attributed to the desorption of physisorbed NH<sub>3</sub>, and NH<sub>3</sub> species desorbed from weak acid sites, medium strength acid sites, and strong acid sites, respectively [7]. Because NH<sub>4</sub><sup>+</sup> ions bonded on Brønsted (B) acid sites are less thermally stable than NH<sub>3</sub> molecules coordinated to Lewis (L) acid sites, it could be concluded that the desorption peaks at low temperature (below 300 °C) can be mainly attributed to NH<sub>4</sub><sup>+</sup> ions bonded on B acid sites, while the desorption peaks at high temperature (above 300 °C) can be related to the desorption of NH<sub>3</sub> molecules from L acid sites [36]. This conclusion can be supported by the results of NH<sub>3</sub>-adsorption *in situ* DRIFTS in Fig. 6. Quantitative analysis data of NH<sub>3</sub>-TPD over these supported ceria-based catalysts are listed in Table 3. Interestingly, it can be seen from this table that the total acid amounts of these catalysts give a sequence of CeO<sub>2</sub>/TiO<sub>2</sub>-R > CeO<sub>2</sub>/TiO<sub>2</sub>-B > CeO<sub>2</sub>/TiO<sub>2</sub>-A. The largest total acid amount of CeO<sub>2</sub>/TiO<sub>2</sub>-R among these supported ceria-based catalysts may be related to the easiest formation of Ti<sup>4+</sup> defects and the strongest interaction between CeO<sub>2</sub> and TiO<sub>2</sub>-R over CeO<sub>2</sub>/TiO<sub>2</sub>-R catalyst, which is beneficial to the adsorption of NH<sub>3</sub> molecules.

Surface acidity of catalysts playing a key role in NH<sub>3</sub>-SCR reaction has been recognized after decades of research. However, this is still controversial whether B acid or L acid is more important. NH<sub>3</sub>-adsorption *in situ* DRIFTS technique is an efficient approach to distinguish B acid and L acid, which is carried out over these supported ceria-based catalysts, as shown in Fig. 6. For CeO<sub>2</sub>/TiO<sub>2</sub>-

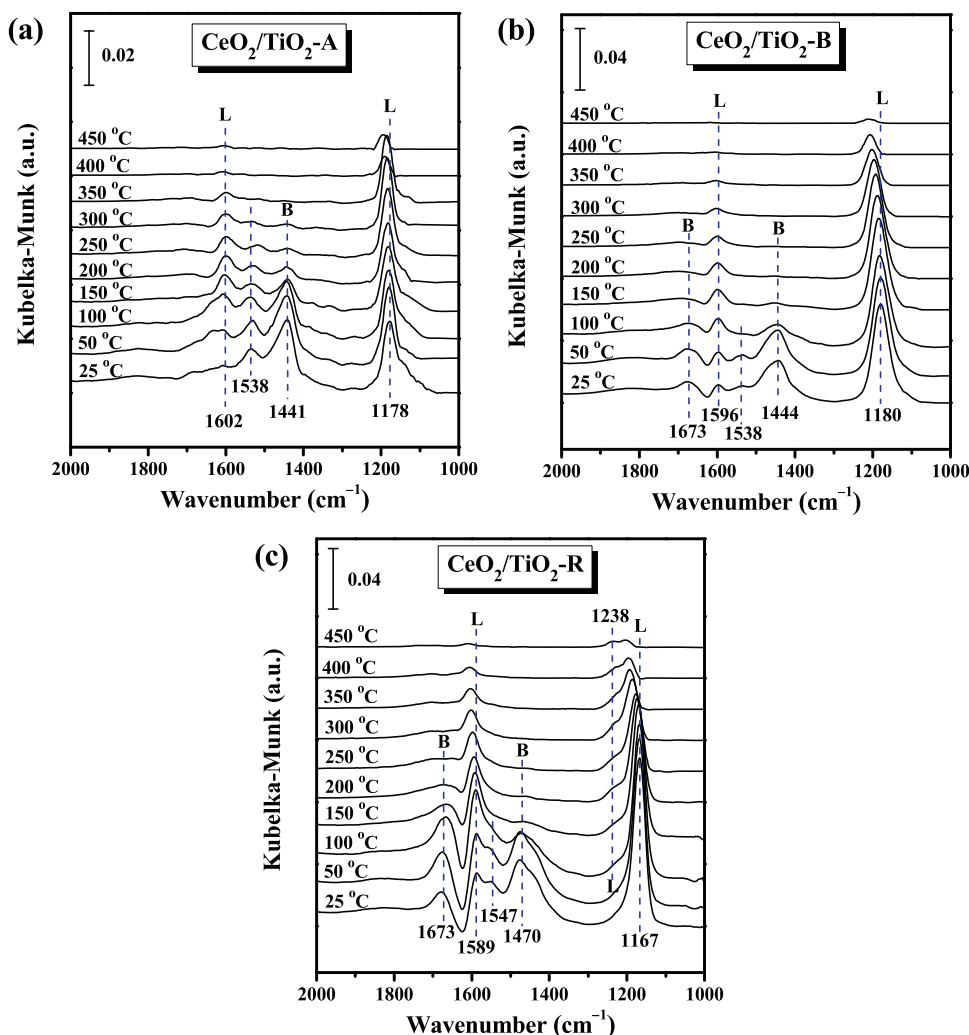


Fig. 6.  $\text{NH}_3$ -adsorption *in situ* DRIFTS of these supported ceria-based catalysts: (a)  $\text{CeO}_2/\text{TiO}_2\text{-A}$ , (b)  $\text{CeO}_2/\text{TiO}_2\text{-B}$ , and (c)  $\text{CeO}_2/\text{TiO}_2\text{-R}$ .

A catalyst (Fig. 6(a)), when it is exposed to  $\text{NH}_3\text{-N}_2$  mixed gases at room temperature ( $25^\circ\text{C}$ ), several IR bands are detected during the wavenumber range of  $1000\text{--}2000\text{ cm}^{-1}$ . According to the literatures [8,9,17,18], the bands at  $1178$  and  $1602\text{ cm}^{-1}$  are attributed to  $\text{NH}_3$  species coordinately adsorbed on L acid sites; while the band at  $1441\text{ cm}^{-1}$  is ascribed to  $\text{NH}_4^+$  ions bonded on B acid sites; interestingly, the weak band at  $1538\text{ cm}^{-1}$  is related to the split  $\nu_3$  mode of bidentate nitrates, which result from the oxidation of the adsorbed  $\text{NH}_3$  species by surface oxygen over  $\text{CeO}_2/\text{TiO}_2\text{-A}$  catalyst. With the increase of temperature, all of these IR bands weakened obviously. Especially, the bands of B acid ( $1441\text{ cm}^{-1}$ ) and bidentate nitrates ( $1538\text{ cm}^{-1}$ ) disappear completely at  $350^\circ\text{C}$  due to the desorption or/and decomposition. However, the bands of L acid ( $1178$  and  $1602\text{ cm}^{-1}$ ) still existed even at  $450^\circ\text{C}$  owing to the strong adsorption for the coordinated  $\text{NH}_3$  species. These phenomena are well consistent with the results of  $\text{NH}_3\text{-TPD}$ .

Similarly, with regard to  $\text{CeO}_2/\text{TiO}_2\text{-B}$  and  $\text{CeO}_2/\text{TiO}_2\text{-R}$  catalysts (Fig. 6(b) and (c)), the bands of L acid, B acid, and bidentate nitrates are also observed at the corresponding positions. Interestingly, a new band appears at  $1673\text{ cm}^{-1}$  over  $\text{CeO}_2/\text{TiO}_2\text{-B}$  and  $\text{CeO}_2/\text{TiO}_2\text{-R}$  catalysts, which is also assigned to  $\text{NH}_4^+$  ions fixed on B acid sites [8,17]. This band may be generated from the reaction of  $\text{NH}_3$  species and the surface hydroxyl group ( $-\text{OH}$ ) adsorbed on the defective sites of  $\text{CeO}_2/\text{TiO}_2\text{-B}$  and  $\text{CeO}_2/\text{TiO}_2\text{-R}$  catalysts. Furthermore, the band of bidentate nitrates over  $\text{CeO}_2/\text{TiO}_2\text{-B}$  and  $\text{CeO}_2/\text{TiO}_2\text{-R}$  catalysts disappears at a lower temperature of  $150^\circ\text{C}$

compared with  $\text{CeO}_2/\text{TiO}_2\text{-A}$  catalyst, indicating the easier desorption or/and decomposition of bidentate nitrates, which is beneficial to the excellent catalytic performance for  $\text{NH}_3\text{-SCR}$  reaction. Especially, with the temperature increases to  $100^\circ\text{C}$ , a new band can be detected at  $1238\text{ cm}^{-1}$  over  $\text{CeO}_2/\text{TiO}_2\text{-R}$  catalyst, which is attributed to  $\text{NH}_3$  species coordinately adsorbed on L acid sites [8,9]. This band may be related to the easiest transfer of  $\text{Ti}^{4+}$  from the lattice of  $\text{TiO}_2\text{-R}$  to the surface of  $\text{CeO}_2/\text{TiO}_2\text{-R}$  catalyst, and then  $\text{NH}_3$  species desorbed from the adjacent acid sites and adsorbed on the coordinately unsaturated  $\text{Ti}^{4+}$  centers, which is conducive to the adsorption and activation of  $\text{NH}_3$  species, and further promotes the progress of  $\text{NH}_3\text{-SCR}$  reaction. Moreover, Fig. 6 exhibits that the band intensity of L acid is remarkably stronger than that of B acid over these supported ceria-based catalysts, and L acid exists in the whole effective temperature range of  $\text{NH}_3\text{-SCR}$  reaction, while B acid disappears at a lower temperature, which indicates that L acid is more important than B acid for  $\text{NH}_3\text{-SCR}$  reaction in the present work.

#### 3.4. Interaction with reactants ( $\text{NO} + \text{NH}_3 + \text{O}_2$ co-adsorption *in situ* DRIFTS)

With the purpose of investigating the interaction between these supported ceria-based catalysts and reactants to further understand the  $\text{NH}_3\text{-SCR}$  reaction mechanism,  $\text{NO} + \text{NH}_3 + \text{O}_2$  co-adsorption *in situ* DRIFTS experiments were carried out. Firstly,

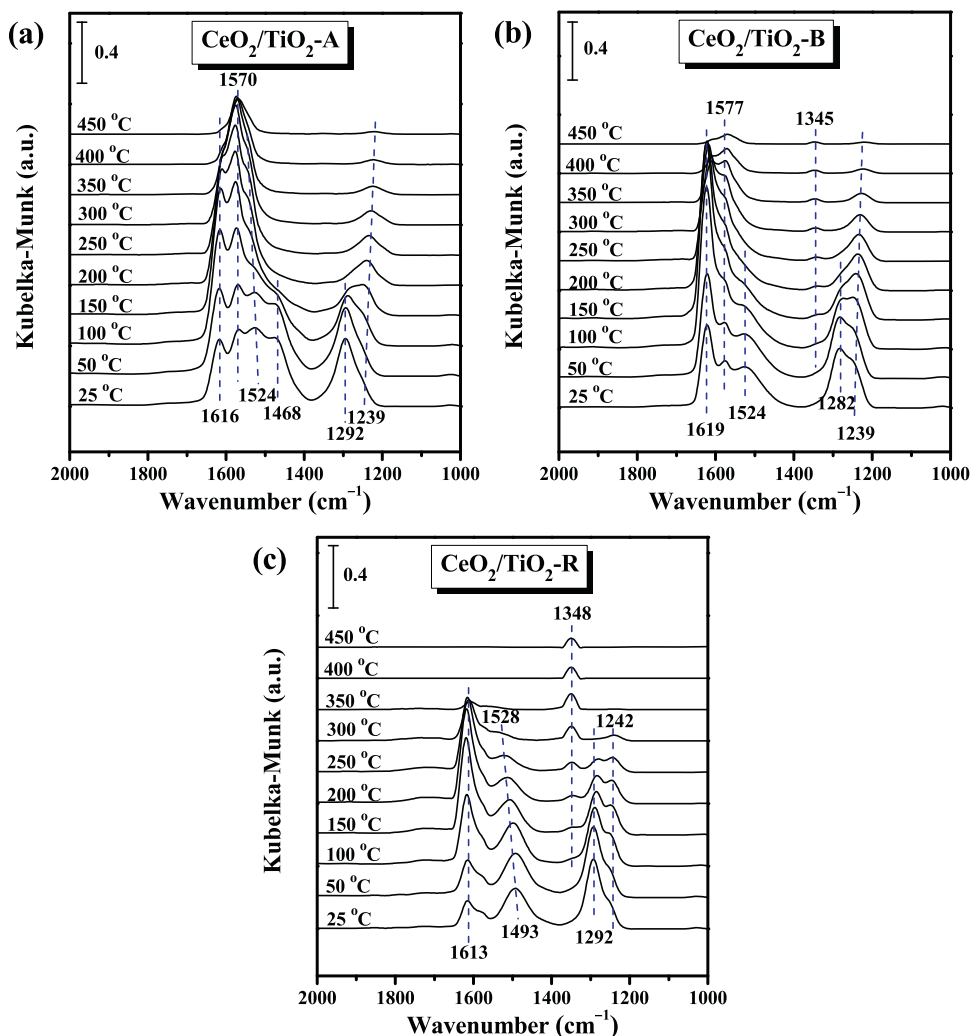
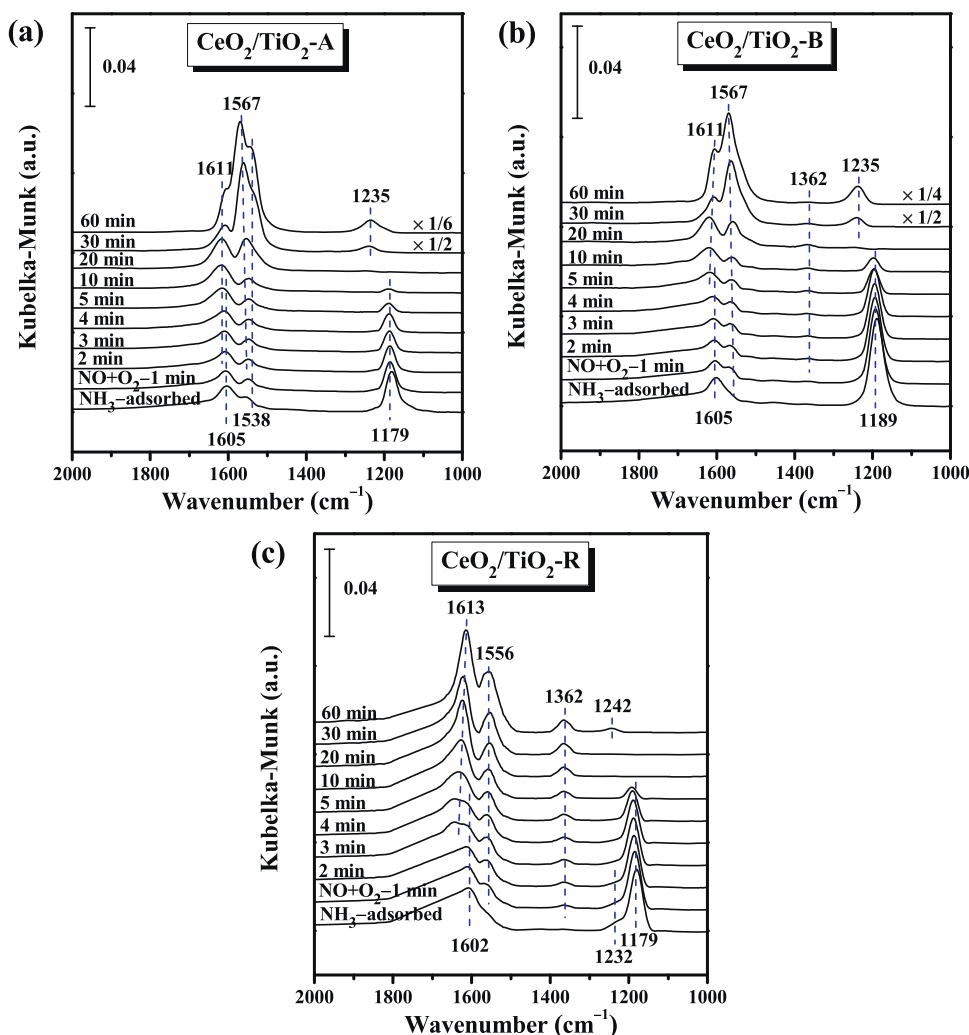


Fig. 7. NO + NH<sub>3</sub> + O<sub>2</sub> co-adsorption *in situ* DRIFTS of these supported ceria-based catalysts: (a) CeO<sub>2</sub>/TiO<sub>2</sub>-A, (b) CeO<sub>2</sub>/TiO<sub>2</sub>-B, and (c) CeO<sub>2</sub>/TiO<sub>2</sub>-R.

the catalyst was placed in an *in situ* DRIFTS cell and pretreated by high purified N<sub>2</sub> at 450 °C for 1 h to remove the physisorbed water. Secondly, the sample background of each target temperature was collected during the cooling process. At room temperature (25 °C), the sample was exposed to NO–NH<sub>3</sub>–O<sub>2</sub>–N<sub>2</sub> mixture (3000 ppm NO, 3000 ppm NH<sub>3</sub>, and 5.0% O<sub>2</sub> by volume) at a rate of 50 ml min<sup>−1</sup> for 1 h to be saturated. Finally, *in situ* DRIFTS were recorded at various target temperatures from room temperature to 450 °C at a rate of 10 °C min<sup>−1</sup> by subtraction of the corresponding sample background. The NO + NH<sub>3</sub> + O<sub>2</sub> co-adsorption *in situ* DRIFTS results of these supported ceria-based catalysts are presented in Fig. 7. With regard to CeO<sub>2</sub>/TiO<sub>2</sub>-A catalyst (Fig. 7(a)), when it is exposed to NO–NH<sub>3</sub>–O<sub>2</sub>–N<sub>2</sub> mixed gases at room temperature (25 °C), several IR vibration bands are detected between 1000 and 2000 cm<sup>−1</sup>. According to the literatures [9,13,37,38], the band at 1616 cm<sup>−1</sup> can be attributed to the bridging bidentate nitrates; the bands at 1570 and 1239 cm<sup>−1</sup> are assigned to the chelating bidentate nitrates; the band at 1524 cm<sup>−1</sup> is related to the split  $\nu_3$  mode of bidentate nitrates; while the bands at 1468 and 1292 cm<sup>−1</sup> can be ascribed to the monodentate nitrates. These results suggest that NO molecules can be also adsorbed on the surface of the supported ceria-based catalyst to generate nitrates. Unfortunately, the IR vibration band intensity of the adsorbed NO<sub>x</sub> species is too strong, so that the IR signals of the adsorbed NH<sub>3</sub> species are covered. Some interesting phenomena can be found during the heating process, the

bands of monodentate nitrates (1468 and 1292 cm<sup>−1</sup>) disappear at 200 °C due to the poor thermal stability; the band intensity of bridging bidentate nitrates (1616 cm<sup>−1</sup>) and chelating bidentate nitrates (1570 and 1239 cm<sup>−1</sup>) increases with the elevation of temperature firstly, and then decreases with the further increase of temperature, which is related to the reaction between the adsorbed NO<sub>x</sub> and NH<sub>3</sub> species, as well as the transformation and dissociation of the adsorbed NO<sub>x</sub> species. However, these bidentate nitrates don't disappear even at 450 °C owing to the strong adsorption.

Similarly, for CeO<sub>2</sub>/TiO<sub>2</sub>-B and CeO<sub>2</sub>/TiO<sub>2</sub>-R catalysts (Fig. 7(b) and (c)), the bands of bridging bidentate nitrates, chelating bidentate nitrates, split  $\nu_3$  mode of bidentate nitrates, and monodentate nitrates are also observed at the corresponding positions. Interestingly, when the temperature increases to 100 °C, a new band appears at 1345–1348 cm<sup>−1</sup> over CeO<sub>2</sub>/TiO<sub>2</sub>-B and CeO<sub>2</sub>/TiO<sub>2</sub>-R catalysts, which can be attributed to the intermediate species generated by the reaction of the adsorbed NO<sub>x</sub> and NH<sub>3</sub> species [37]. This phenomenon suggests that the catalytic performance of CeO<sub>2</sub>/TiO<sub>2</sub>-B and CeO<sub>2</sub>/TiO<sub>2</sub>-R catalysts maybe better than that of CeO<sub>2</sub>/TiO<sub>2</sub>-A catalyst for NH<sub>3</sub>-SCR reaction. Furthermore, with regard to CeO<sub>2</sub>/TiO<sub>2</sub>-R catalyst, all of the bridging bidentate nitrates, chelating bidentate nitrates, split  $\nu_3$  mode of bidentate nitrates, and monodentate nitrates disappear completely at 400 °C. The reason maybe that the strongest interaction between CeO<sub>2</sub> and TiO<sub>2</sub>-R over CeO<sub>2</sub>/TiO<sub>2</sub>-R catalyst and its best reduction property



**Fig. 8.** Time-resolved  $\text{NO} + \text{O}_2$  adsorption *in situ* DRIFTS of these supported ceria-based catalysts pre-adsorbed  $\text{NH}_3$  at  $300^\circ\text{C}$ : (a)  $\text{CeO}_2/\text{TiO}_2\text{-A}$ , (b)  $\text{CeO}_2/\text{TiO}_2\text{-B}$ , and (c)  $\text{CeO}_2/\text{TiO}_2\text{-R}$ .

cause the back-donation of electrons to the anti-bonding orbit of  $\text{NO}_x$  species, which can weaken the N–O bond, and further promote the reaction of the adsorbed  $\text{NO}_x$  and  $\text{NH}_3$  species, as well as the transformation and dissociation of the adsorbed  $\text{NO}_x$  species, and consequently result in excellent catalytic performance.

Indeed, the IR vibration band intensity of the adsorbed  $\text{NO}_x$  species over these supported ceria-based catalysts is too strong, which leads to that the IR signals of the adsorbed  $\text{NH}_3$  species are covered. Therefore, in order to investigate the reaction between the adsorbed  $\text{NH}_3$  and  $\text{NO}_x$  species intuitively, time-resolved  $\text{NO} + \text{O}_2$  adsorption *in situ* DRIFTS of these supported ceria-based catalysts pre-adsorbed  $\text{NH}_3$  at  $300^\circ\text{C}$  were carried out, and the corresponding results are displayed in Fig. 8. It can be seen from Fig. 8(a) that when  $\text{CeO}_2/\text{TiO}_2\text{-A}$  catalyst is saturated by  $\text{NH}_3$  at  $300^\circ\text{C}$ , the bands of L acid ( $1605$  and  $1179\text{ cm}^{-1}$ ) and split  $\nu_3$  mode of bidentate nitrates ( $1538\text{ cm}^{-1}$ ) can be detected. Then,  $\text{NH}_3$  gas is cut off, and  $\text{NO} + \text{O}_2$  gas is switched on. We can find that the band intensity of L acid ( $1605$  and  $1179\text{ cm}^{-1}$ ) weakens obviously with the increase of  $\text{NO} + \text{O}_2$  injection time, and disappears completely at 20 min. However, with the increase of  $\text{NO} + \text{O}_2$  injection time, the band intensity of split  $\nu_3$  mode of bidentate nitrates ( $1538\text{ cm}^{-1}$ ) strengthens remarkably, and some new IR signals of bridging bidentate nitrates ( $1611\text{ cm}^{-1}$ ) and chelating bidentate nitrates ( $1567$  and  $1235\text{ cm}^{-1}$ ) can be observed. These phenomena suggest that

the adsorbed  $\text{NH}_3$  species can react with the adsorbed  $\text{NO}_x$  species efficiently.

Furthermore, only L acid can be detected over  $\text{CeO}_2/\text{TiO}_2\text{-B}$  and  $\text{CeO}_2/\text{TiO}_2\text{-R}$  catalysts (Fig. 8(b) and (c)) when they are saturated by  $\text{NH}_3$  at  $300^\circ\text{C}$ . The change trend of L acid, bridging bidentate nitrates, and chelating bidentate nitrates with the increase of  $\text{NO} + \text{O}_2$  injection time over  $\text{CeO}_2/\text{TiO}_2\text{-B}$  and  $\text{CeO}_2/\text{TiO}_2\text{-R}$  catalysts is similar to that of  $\text{CeO}_2/\text{TiO}_2\text{-A}$  catalyst. However, an intermediate species generated by the reaction of the adsorbed  $\text{NO}_x$  and  $\text{NH}_3$  species can be detected at  $1362\text{ cm}^{-1}$  over  $\text{CeO}_2/\text{TiO}_2\text{-B}$  and  $\text{CeO}_2/\text{TiO}_2\text{-R}$  catalysts when  $\text{NO} + \text{O}_2$  is introduced, which suggests that the catalytic performance of  $\text{CeO}_2/\text{TiO}_2\text{-B}$  and  $\text{CeO}_2/\text{TiO}_2\text{-R}$  catalysts maybe better than that of  $\text{CeO}_2/\text{TiO}_2\text{-A}$  catalyst for  $\text{NH}_3\text{-SCR}$  reaction. Moreover, we find that only L acid can be detected over these supported ceria-based catalysts when they are saturated by  $\text{NH}_3$  at  $300^\circ\text{C}$ , while B acid is absent. However, all of these supported ceria-based catalysts exhibit high catalytic activity (above 80%) for  $\text{NH}_3\text{-SCR}$  reaction at  $300^\circ\text{C}$  (see Fig. 10). These phenomena suggest that L acid is more important than B acid for  $\text{NH}_3\text{-SCR}$  reaction in the present work.

### 3.5. Surface analysis (XPS)

It is well known that surface composition and oxidation states of catalysts are very important for  $\text{NH}_3\text{-SCR}$  reaction, which can



**Table 4**  
Surface composition and atomic ratio of these supported ceria-based catalysts calculated from XPS.

Catalysts	Atomic concentration (at.%)			Atomic ratio (%)		
	Ce	Ti	O	Ce/(Ce + Ti)	Ce <sup>3+</sup> /(Ce <sup>3+</sup> + Ce <sup>4+</sup> )	O <sup>2−</sup> /(O <sup>2−</sup> + O <sup>•</sup> )
CeO <sub>2</sub> /TiO <sub>2</sub> -A	1.22	26.53	72.25	4.40	27.15	25.80
CeO <sub>2</sub> /TiO <sub>2</sub> -B	1.71	26.85	71.44	5.99	33.37	27.97
CeO <sub>2</sub> /TiO <sub>2</sub> -R	2.26	26.62	71.12	7.83	35.29	28.43

remarkably influence the adsorption and activation of reactant molecules. Therefore, the surface properties of these supported ceria-based catalysts are investigated by XPS, and the corresponding results are displayed in Fig. 9. It can be seen from Fig. 9(a) that the complex Ce 3d spectra of CeO<sub>2</sub>/TiO<sub>2</sub>-A, CeO<sub>2</sub>/TiO<sub>2</sub>-B, and CeO<sub>2</sub>/TiO<sub>2</sub>-R catalysts are fitted with eight binding energy peaks, labeled as u''', u'', u', u<sup>0</sup> (u), and v''', v'', v', v<sup>0</sup> (v), respectively. According to the literatures [11,20,32,39–41], u' and v' are attributed to surface Ce<sup>3+</sup> species, while the other six binding energy peaks are ascribed to the full oxidation state Ce<sup>4+</sup>, which indicate that both of Ce<sup>3+</sup> and Ce<sup>4+</sup> species co-exist on the surface of these supported ceria-based catalysts. The appearance of surface Ce<sup>3+</sup> species is bound to result in the formation of oxygen vacancy, which is beneficial to the dissociation of NO molecules, and further promotes the enhancement of catalytic performance for NH<sub>3</sub>-SCR reaction. Therefore, the content of surface Ce<sup>3+</sup> over these supported ceria-based catalysts is calculated by the following equation [42,43], and listed in Table 4.

$$\text{Ce}^{3+} (\%) = \frac{S_{u''} + S_{v''}}{\sum (S_u + S_v)} \times 100$$

Table 4 exhibits that the content of surface Ce<sup>3+</sup> over these supported ceria-based catalysts is in the order of CeO<sub>2</sub>/TiO<sub>2</sub>-R > CeO<sub>2</sub>/TiO<sub>2</sub>-B > CeO<sub>2</sub>/TiO<sub>2</sub>-A, which may be related to the interaction between CeO<sub>2</sub> and TiO<sub>2</sub>, as well as the dispersion of CeO<sub>2</sub> on the surface of TiO<sub>2</sub>. It is widely reported that there is some strong interaction between CeO<sub>2</sub> and TiO<sub>2</sub> over CeO<sub>2</sub>/TiO<sub>2</sub> catalysts through the transfer of electrons [13–15,37]. However, anatase, brookite, and rutile TiO<sub>2</sub> have different surface atomic arrangement structures, which can influence the difficulty degree of electron transfer, and further lead to different content of surface Ce<sup>3+</sup>. Furthermore, it can be seen from Table 4 that the value of Ce/(Ce + Ti) is ranked by CeO<sub>2</sub>/TiO<sub>2</sub>-R > CeO<sub>2</sub>/TiO<sub>2</sub>-B > CeO<sub>2</sub>/TiO<sub>2</sub>-A, which indicates that the dispersion of CeO<sub>2</sub> on the surface of TiO<sub>2</sub>-R is the best, while on the surface of TiO<sub>2</sub>-A is the worst. Some researchers reported that the content of surface Ce<sup>3+</sup> in the particles increases with the decrease of crystallite size [44,45], which suggests that the dispersion of CeO<sub>2</sub> on the surface of TiO<sub>2</sub> can also affect the surface Ce<sup>3+</sup> content of these supported ceria-based catalysts.

Fig. 9(b) presents Ti 2p spectra of these supported ceria-based catalysts. The binding energy peak of Ti 2p<sub>3/2</sub> can be observed at 458.2, 458.0, and 458.0 eV over CeO<sub>2</sub>/TiO<sub>2</sub>-A, CeO<sub>2</sub>/TiO<sub>2</sub>-B, and CeO<sub>2</sub>/TiO<sub>2</sub>-R catalysts, respectively, which is slightly lower than that of Ti<sup>4+</sup> (458.4 eV) in pure TiO<sub>2</sub> [13,46]. This phenomenon suggests that a small amount of Ti<sup>3+</sup> may exist accompanied by Ti<sup>4+</sup> on the surface of these supported ceria-based catalysts due to the interaction between CeO<sub>2</sub> and TiO<sub>2</sub> through Ce-O-Ti bridge bonds (i.e., the electron transfer of Ce<sup>3+</sup> + Ti<sup>4+</sup> ↔ Ce<sup>4+</sup> + Ti<sup>3+</sup> shifts to right). Furthermore, we can find that Ti 2p<sub>3/2</sub> binding energy peak of CeO<sub>2</sub>/TiO<sub>2</sub>-B and CeO<sub>2</sub>/TiO<sub>2</sub>-R catalysts is lower than that of CeO<sub>2</sub>/TiO<sub>2</sub>-A catalyst, which indicates that the electron transfer between Ce and Ti ions in CeO<sub>2</sub>/TiO<sub>2</sub>-B and CeO<sub>2</sub>/TiO<sub>2</sub>-R catalysts is easier than that in CeO<sub>2</sub>/TiO<sub>2</sub>-A catalyst. It seems to be contradictory with the order of surface Ce<sup>3+</sup> content (CeO<sub>2</sub>/TiO<sub>2</sub>-R > CeO<sub>2</sub>/TiO<sub>2</sub>-B > CeO<sub>2</sub>/TiO<sub>2</sub>-A). In actual fact, this unusual phenomenon can be interpreted by

the formation of surface oxygen vacancy to maintain the charge balance.

O 1s spectra of these supported ceria-based catalysts are fitted with two components, as shown in Fig. 9(c). All of them exhibit a strong binding energy peak at 529.3 eV and a shoulder around 530.9 eV, labeled as O' and O'', which can be attributed to the lattice oxygen, and surface adsorbed oxygen species fixed on defective sites (such as oxygen vacancy), respectively [9,13,17]. It is well known that the surface adsorbed oxygen species is beneficial to the oxidation of NO to NO<sub>2</sub>, and further promotes the progress of NH<sub>3</sub>-SCR reaction through a “fast SCR” route [9]. Therefore, the content of surface adsorbed oxygen species (expressed as O''/(O' + O'')) over these supported ceria-based catalysts is calculated and listed in Table 4. It can be seen from this table that the value of O''/(O' + O'') is ranked by CeO<sub>2</sub>/TiO<sub>2</sub>-R > CeO<sub>2</sub>/TiO<sub>2</sub>-B > CeO<sub>2</sub>/TiO<sub>2</sub>-A, which is consistent with the order of surface Ce<sup>3+</sup> content.

### 3.6. Catalytic performance and H<sub>2</sub>O + SO<sub>2</sub> resistance (NH<sub>3</sub>-SCR model reaction)

The catalytic performance of these TiO<sub>2</sub> supports and the corresponding supported ceria-based catalysts is evaluated by NH<sub>3</sub>-SCR model reaction, and the corresponding results are given in Fig. 10. It can be seen from Fig. 10(a) that NO<sub>x</sub> conversion of these samples is strongly dependent on the reaction temperature. With regard to these TiO<sub>2</sub> supports, they exhibit poor reactivity below 300 °C. However, the reactivity of these TiO<sub>2</sub> supports increases obviously when the reaction temperature is higher than 300 °C, and gives a sequence of TiO<sub>2</sub>-R > TiO<sub>2</sub>-B > TiO<sub>2</sub>-A, which may be related to the different surface atomic arrangement structures and the formation difficulty degree of defective sites over these TiO<sub>2</sub> supports. In addition, we can find that NO<sub>x</sub> conversion of these supported ceria-based catalysts is remarkably higher than that of TiO<sub>2</sub>-A, TiO<sub>2</sub>-B, and TiO<sub>2</sub>-R supports due to the interaction between CeO<sub>2</sub> and TiO<sub>2</sub> through the formation of Ce-O-Ti species. The reactivity of these supported ceria-based catalysts can be ranked by CeO<sub>2</sub>/TiO<sub>2</sub>-R > CeO<sub>2</sub>/TiO<sub>2</sub>-B > CeO<sub>2</sub>/TiO<sub>2</sub>-A, which is consistent with the order of reduction property, acid amount, surface Ce<sup>3+</sup> content, and surface adsorbed oxygen species. Furthermore, all of these supported ceria-based catalysts present similar volcano-type reactivity curves, i.e., the reactivity increases with the elevation of reaction temperature firstly, and then declines with further increase of reaction temperature due to the non-selective oxidation of reductant NH<sub>3</sub> molecules. Especially, CeO<sub>2</sub>/TiO<sub>2</sub>-R catalyst exhibits high NO<sub>x</sub> conversion (above 80%) during a wide operating temperature window of 200–400 °C due to the most excellent reduction property as well as the largest amounts of acid sites, surface Ce<sup>3+</sup> content, and surface adsorbed oxygen species among these supported ceria-based catalysts, which result from the strongest interaction between CeO<sub>2</sub> and TiO<sub>2</sub>-R. The most excellent reduction property and the largest amount of surface adsorbed oxygen species are beneficial to the oxidation of NO to NO<sub>2</sub>, which can promote the progress of NH<sub>3</sub>-SCR reaction through a “fast SCR” route. On the other hand, the formation of oxygen vacancy accompanied by surface Ce<sup>3+</sup> and the consumption of surface oxygen species is conducive to the dissociation of NO molecules. Moreover, the largest amount of acid sites can promote the adsorption and activation of

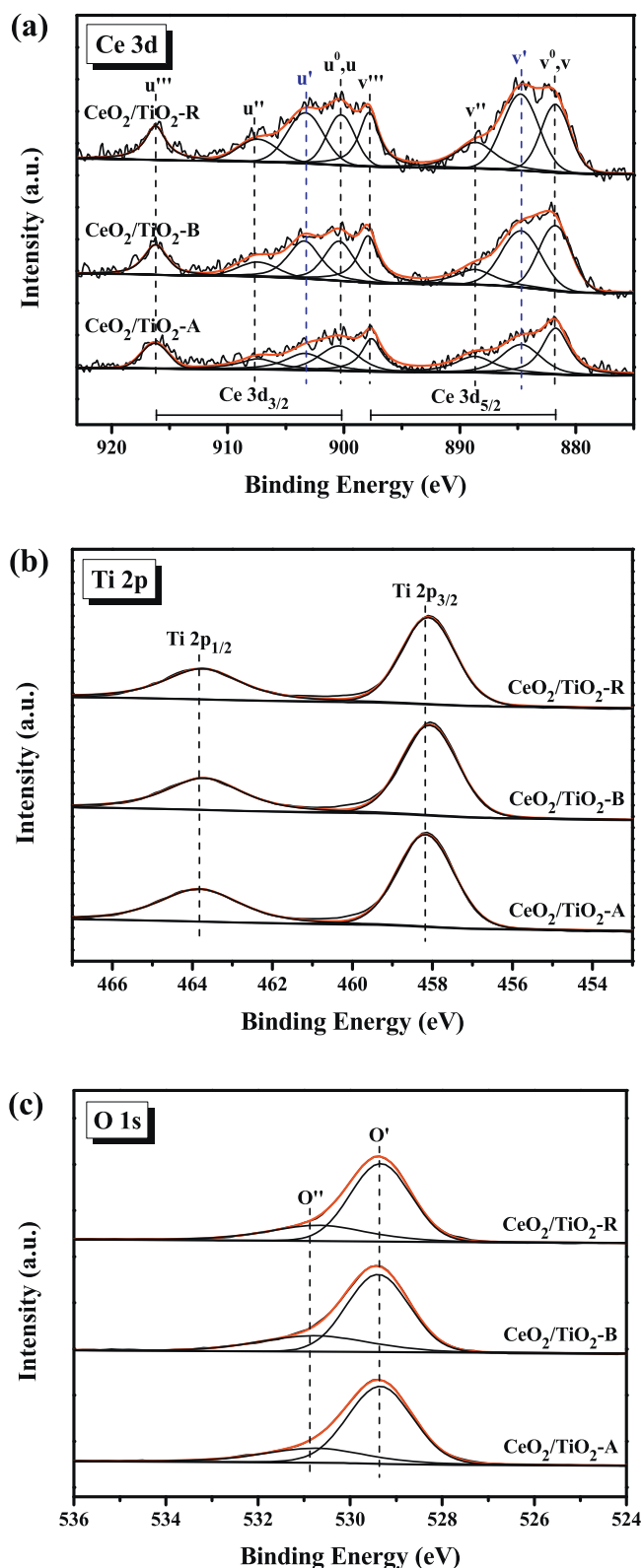


Fig. 9. XPS results of these supported ceria-based catalysts: (a) Ce 3d, (b) Ti 2p, and (c) O 1s.

NH<sub>3</sub> species, efficiently. All of these are beneficial to the enhancement of catalytic performance for NH<sub>3</sub>-SCR reaction.

Furthermore, N<sub>2</sub>O is a main by-product of NH<sub>3</sub>-SCR reaction, which usually generates from the non-selective oxidation of NH<sub>3</sub> and partial reduction of NO<sub>x</sub>, and can also cause serious

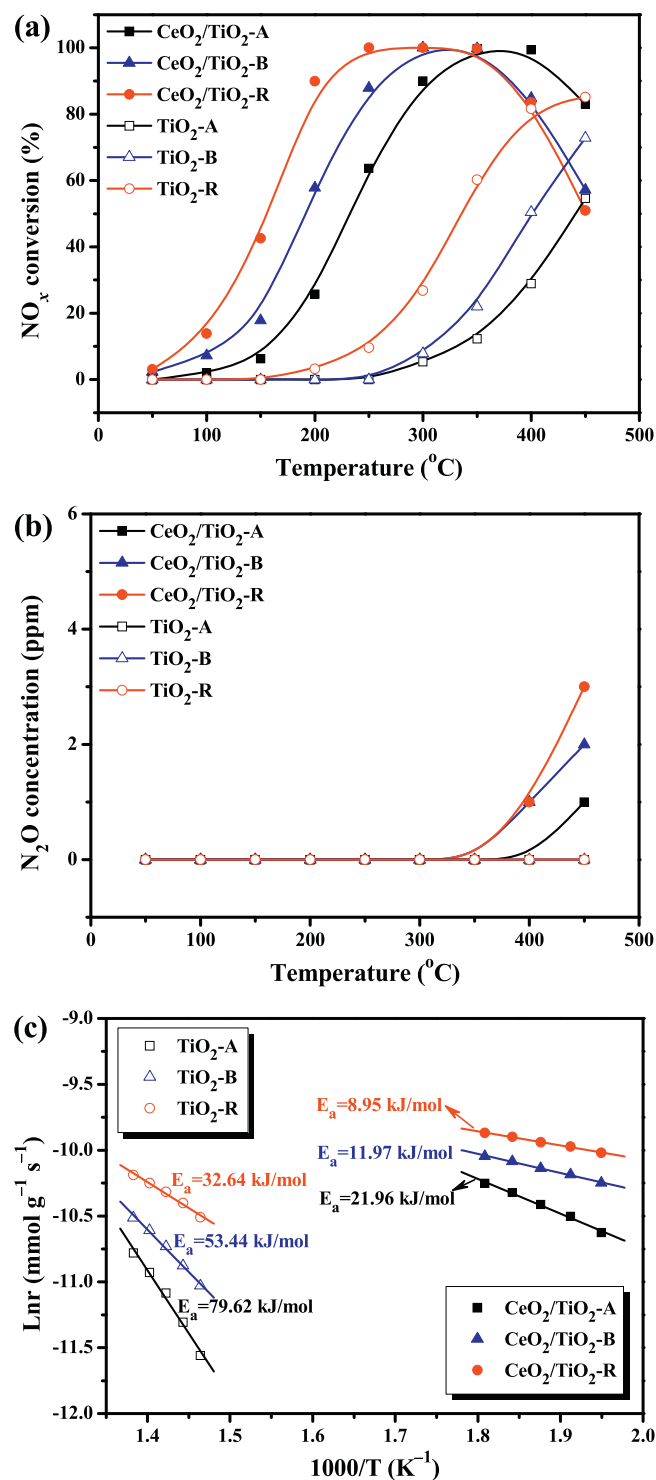


Fig. 10. (a) NO<sub>x</sub> conversion, (b) N<sub>2</sub>O concentration, and (c) Arrhenius plots of these supports and the corresponding supported ceria-based catalysts.

atmospheric pollution [47,48]. So, the generated N<sub>2</sub>O concentration attracts more attention in NH<sub>3</sub>-SCR reaction. In the present work, the generated N<sub>2</sub>O concentration over these TiO<sub>2</sub> supports and the corresponding supported ceria-based catalysts was detected during the whole reaction temperature range (50–450 °C), and the corresponding results are exhibited in Fig. 10(b). We can find that N<sub>2</sub>O concentration of these samples is very small (i.e., not higher than 3 ppm) in the temperature range of 50–450 °C, which can be

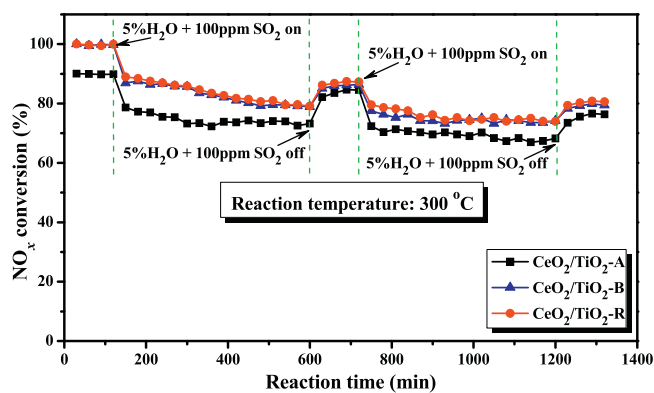


Fig. 11. Water and sulfur resistance of these supported ceria-based catalysts at 300 °C.

ignored. This phenomenon suggests that these samples have high selectivity for the catalytic reduction of  $\text{NO}_x$  to  $\text{N}_2$ .

With the purpose of further understanding the difference of catalytic performance among these  $\text{TiO}_2$  supports and the corresponding supported ceria-based catalysts, the apparent activation energy ( $E_a$ ) of  $\text{NH}_3$ -SCR reaction over these samples is investigated according to Arrhenius equation, as shown in Fig. 10(c). It is widely reported that  $\text{NH}_3$ -SCR reaction over ceria-based catalysts is approximately first-order for  $\text{NO}_x$  and zero-order for  $\text{NH}_3$  [12,49]. Therefore,  $E_a$  can be determined by the slope of Arrhenius plots with lower  $\text{NO}_x$  conversion (below 30%, in order to exclude the influence of diffusion) based on pseudo first-order reaction kinetic equation. Fig. 10(c) exhibits that the value of  $E_a$  over these supported ceria-based catalysts is in the order of  $\text{CeO}_2/\text{TiO}_2\text{-A}$  ( $21.96 \text{ kJ mol}^{-1}$ ) >  $\text{CeO}_2/\text{TiO}_2\text{-B}$  ( $11.97 \text{ kJ mol}^{-1}$ ) >  $\text{CeO}_2/\text{TiO}_2\text{-R}$  ( $8.95 \text{ kJ mol}^{-1}$ ), which is owing to the different surface atomic arrangement structures of  $\text{TiO}_2\text{-A}$ ,  $\text{TiO}_2\text{-B}$ , and  $\text{TiO}_2\text{-R}$ , as well as the different interaction between  $\text{CeO}_2$  and  $\text{TiO}_2$  (anatase, brookite, and rutile). This observation indicates that  $\text{NH}_3$ -SCR reaction over these supported ceria-based catalysts follows different reaction routes, and the occurrence over  $\text{CeO}_2/\text{TiO}_2\text{-R}$  catalyst is the easiest, which is in well agreement with the results of  $\text{NO}_x$  conversion. Moreover, the value of  $E_a$  over these supported ceria-based catalysts is obviously smaller than that of  $\text{TiO}_2\text{-A}$  ( $79.62 \text{ kJ mol}^{-1}$ ),  $\text{TiO}_2\text{-B}$  ( $53.44 \text{ kJ mol}^{-1}$ ), and  $\text{TiO}_2\text{-R}$  ( $32.64 \text{ kJ mol}^{-1}$ ) supports, which suggests that the loading of  $\text{CeO}_2$  can efficiently decrease the energy barrier of  $\text{NH}_3$ -SCR reaction.

The existence of  $\text{H}_2\text{O}$  and  $\text{SO}_2$  is unavoidable in the practical application of denitration catalysts. Therefore, the water and sulfur resistance of these supported ceria-based catalysts are explored for  $\text{NH}_3$ -SCR reaction, and the reaction temperature is fixed at 300 °C, the corresponding results are displayed in Fig. 11. We can find that  $\text{NO}_x$  conversion of  $\text{CeO}_2/\text{TiO}_2\text{-A}$ ,  $\text{CeO}_2/\text{TiO}_2\text{-B}$ , and  $\text{CeO}_2/\text{TiO}_2\text{-R}$  catalysts is very stable in the absence of  $\text{H}_2\text{O}$  and  $\text{SO}_2$ . However, it declines to some extent when  $\text{H}_2\text{O}$  (5%) and  $\text{SO}_2$  (100ppm) are introduced. Interestingly,  $\text{NO}_x$  conversion can be partially recovered after cutting off the injection of  $\text{H}_2\text{O}$  and  $\text{SO}_2$ . Moreover, the catalytic activity of these supported ceria-based catalysts further decreases when  $\text{H}_2\text{O}$  and  $\text{SO}_2$  are injected repeatedly, while it can be also partially recovered with the removal of  $\text{H}_2\text{O}$  and  $\text{SO}_2$ . These phenomena indicate that  $\text{H}_2\text{O}$  and  $\text{SO}_2$  can result in the reversible and irreversible deactivation of  $\text{CeO}_2/\text{TiO}_2\text{-A}$ ,  $\text{CeO}_2/\text{TiO}_2\text{-B}$ , and  $\text{CeO}_2/\text{TiO}_2\text{-R}$  catalysts, which may be related to the competitive adsorption of  $\text{H}_2\text{O}$  and  $\text{NH}_3$ , the deposition of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$ , as well as the sulfation of active components [10,17,50]. Furthermore, Fig. 11 shows that  $\text{NO}_x$  conversion of  $\text{CeO}_2/\text{TiO}_2\text{-B}$  and  $\text{CeO}_2/\text{TiO}_2\text{-R}$  catalysts is higher than that of  $\text{CeO}_2/\text{TiO}_2\text{-A}$  catalyst in the presence of  $\text{H}_2\text{O}$  and  $\text{SO}_2$ , but the decrease of  $\text{NO}_x$  conversion

over  $\text{CeO}_2/\text{TiO}_2\text{-A}$  catalyst caused by  $\text{H}_2\text{O}$  and  $\text{SO}_2$  poisoning is the most slight among these supported ceria-based catalysts, which suggests that the tolerance of  $\text{H}_2\text{O}$  and  $\text{SO}_2$  over  $\text{CeO}_2/\text{TiO}_2\text{-B}$  and  $\text{CeO}_2/\text{TiO}_2\text{-R}$  catalysts still needs to be further enhanced.

#### 4. Conclusions

In summary, a comparative study of  $\text{CeO}_2/\text{TiO}_2\text{-A}$ ,  $\text{CeO}_2/\text{TiO}_2\text{-B}$ , and  $\text{CeO}_2/\text{TiO}_2\text{-R}$  catalysts is carried out with the purpose of clarifying the influence of  $\text{TiO}_2$  supports with different crystal forms on the physicochemical properties and catalytic performance of these supported ceria-based catalysts for  $\text{NH}_3$ -SCR reaction. The obtained results indicate that  $\text{CeO}_2$  species is highly dispersed on the surface of  $\text{TiO}_2\text{-A}$ ,  $\text{TiO}_2\text{-B}$ , and  $\text{TiO}_2\text{-R}$  supports, and strongly interacts with these  $\text{TiO}_2$  supports. However, because of the different surface atomic arrangement structures of  $\text{TiO}_2\text{-A}$ ,  $\text{TiO}_2\text{-B}$ , and  $\text{TiO}_2\text{-R}$  supports, the interaction between  $\text{CeO}_2$  and  $\text{TiO}_2$  depends on the crystal form of  $\text{TiO}_2$ , which leads to that the reduction property, acid amount, surface  $\text{Ce}^{3+}$  content, surface adsorbed oxygen species, and catalytic performance of these supported ceria-based catalysts are different from each other. Furthermore,  $\text{CeO}_2/\text{TiO}_2\text{-R}$  catalyst exhibits the best physicochemical property and optimal catalytic performance for  $\text{NH}_3$ -SCR reaction, but its tolerance of  $\text{H}_2\text{O}$  and  $\text{SO}_2$  still needs to be further improved. Therefore, we will focus on the enhancement of water and sulfur resistance of  $\text{CeO}_2/\text{TiO}_2\text{-R}$  catalyst in the near future.

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